

Table IV.

	I. $t$ .	II. $d_d'$ .	III. $n_D'$ .	IV. $t_c$ .	V. $d_c$ .	VI. $n_c$ .	VII. Percentage difference.
Hydrogen iodide (liquid)	12	2.270	1.466	150.7	—	1.162	+ 3.2
Hydrogen chloride (gas)	0	0.0016282	1.000447	52.3	0.61	1.173	+ 4.2
Bromine (vapour)	0	0.0071412	1.001132	302.2	1.18	1.194	+ 6.0
Chloroform (liquid)	20	1.4896	1.44621	260	—	1.142	+ 1.4
Ethylidene dichlo- ride (liquid)	0	1.2069	1.42881	250	0.419	1.138	+ 1.0
Carbon tetrachlo- ride	12.3	1.6095	1.4656	283.15	0.5576	1.148	+ 1.9
Tin tetrachloride	20	2.231	1.5124	318.7	—	1.154	+ 2.5
Benzene .....	20.2	0.8788	1.50054	288.5	0.3045	1.157	+ 2.7
Chlorobenzene ...	15	1.1019	1.5268	360	0.3654	1.157	+ 2.7
Bromobenzene ...	13.2	1.5084	1.5635	397	0.4853	1.162	+ 3.2
Iodobenzene .....	8	1.8482	1.62707	448	0.5814	1.173	+ 4.2

of light and the electronic theory of the constitution of matter. These developments, however, are reserved for later treatment, after the fundamental assumption has been tested by experiment.

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*Optical Investigation of Crystallised Nitrogen, Argon, Methane,  
and some of the simpler Organic Compounds, of Low Melting  
Points.*

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Nothing is known about the crystallographic properties of the elements gaseous at ordinary temperatures and of many of the most simply constituted organic bodies. As it is not probable that the preparation of well-developed single crystals, nor the measurement of such crystals by the methods now used for crystal measurements, would be successful, some observations on the solid forms of these bodies by crystallo-optical methods have been undertaken and will be described in this paper. The experimental difficulties are too great to permit of an investigation as complete as that which may be undertaken with substances crystallising at ordinary temperatures, but in spite of the fragmental character of the results obtained, they throw

light upon the general crystallographic properties of these substances, and may for certain general purposes be sufficient.

*Methods of Investigation and Apparatus.*

Of the two methods employed at ordinary temperatures for crystallo-optical investigations, namely that of cutting thin sections of the crystal in certain directions, and that of allowing the substance to crystallise in a thin layer between a slide and a covering glass under the polarisation microscope, only the latter method can be adopted for work at low temperatures. As the gas has first to be condensed to a liquid between the glass plates, and has then to be crystallised, I first tried to obtain a suitable crystallisation vessel by blowing a small bulb on to a glass tube and squeezing the bulb flat while the glass was still soft.

A few experiments with nitrogen were made in crystallisation vessels of this kind, but as it is not possible to obtain vessels with perfectly flat surfaces the crystal growth cannot be seen sufficiently clearly under the microscope. Besides, these glass vessels usually crack if they are made so narrow that the walls nearly touch each other. I therefore started to make the crystallisation vessels out of quartz-glass bulbs. As, however, polished quartz-glass plates—unlike glass plates for optical work—may be sealed to any piece of quartz glass without cracking, I managed to make a small extremely narrow vessel with polished surfaces by placing a ring-shaped piece of iridium foil, 0.02 mm. thick, between two round quartz-glass plates, 15 mm. in diameter and 0.8 mm. thick, and melting the edges of the two plates together before the oxygen blowpipe, except at one point, where they were widened out to form a funnel-shaped opening to the flat interior space between the plates. A small quartz-glass tube was then sealed to the plates at this point, the tube thus forming a kind of neck to the bottle-shaped vessel.

A difficulty arose on account of the iridium evaporating to some extent and condensing on parts of the inner surfaces of the quartz-glass plates during the process of melting together the edges of these plates. Subsequently Mr. Lascelles (of the Silica Syndicate, Hatton Garden, E.C.) kindly undertook to prepare more of these vessels for me. After some tests it was found preferable to fit the two quartz glass plates to each other by adding molten quartz glass to the edges instead of melting them together. The quartz glass plates then get less hot and a thin platinum wire can be used to keep the discs apart during the process of fixing the plates to each other, instead of the iridium foil. When the plates have been sealed together in this way, the platinum wire is drawn out of the vessel and a piece of quartz-glass tube, forming the neck of the flat bottle, attached to it.

In this way it is possible to manufacture vessels with a nearly "plane-parallel" space between the polished surfaces, these being from 0.05 mm. upwards apart, according to the size of the platinum wire employed. The thickness of the layer of the substance crystallising inside such a crystallisation vessel is thus equal to that of the thicker "thin sections" of rocks used in petrographical investigations, and many of the same crystallo-optical methods may therefore be employed with advantage in studying crystallisations in these quartz-glass vessels. Fig. 1 shows one of these vessels in front and in side view.\*

In the investigation of substances liquid at ordinary temperatures, a few drops of the liquid are brought into the stem of the vessel, the air from the flat space between the plates is expelled, and the liquid sucked into this by alternately gently heating and cooling the plates a few times. The most effective way to clean the vessel has been found to be by sucking in a few drops of concentrated sulphuric acid, heating and evaporating this, and finally slightly igniting the whole piece of apparatus. If the apparatus is strongly heated directly after having contained some organic liquid, carbon is deposited, which can only be removed by repeated treatment with hot concentrated sulphuric acid. In the case of gases, a T-piece is attached to the neck of the vessel by means of a piece of rubber pressure tubing, and the other ends of the T-piece connected with the gasholder, and with an air-pump. After the apparatus has been exhausted, it is sealed-off from the pump, and the gas from the gasholder is permitted to enter. The vessel is cooled until the gas liquefies between the plates, and the liquid is then crystallised by further cooling.

In the case of methane and argon, it was sufficient to cool the crystallisation vessel by keeping it inside a small vacuum vessel containing a few cubic centimetres of liquid air at the bottom, and evaporating this under exhaust. Through a syphon fresh quantities of liquid air could be admitted to the vacuum vessel. The crystals were observed through slits

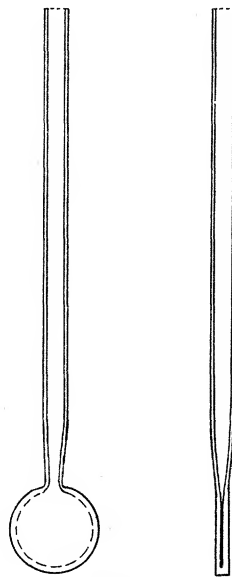


FIG. 1.

\* The vessels were originally constructed in order to be used inside a high-pressure bomb to hold liquids which attack rubber, although they have first been employed for the purposes of this investigation. The author intends to measure the absorption spectra of sulphur at high temperatures, and of bromine at low temperatures, with the aid of these same vessels.

in the silvering of the vacuum vessel by means of an ordinary polarisation microscope clamped in horizontal position. In the case of nitrogen, it was necessary to employ a slightly more complicated apparatus in order to be able to exhaust also the liquid nitrogen contained in the crystallisation vessel. This arrangement is described below in connection with the data concerning nitrogen.

The organic liquids crystallising below  $-100^{\circ}$  were cooled in the same way as methane. In the case of those crystallising at higher temperatures, the lower half of the silvered vacuum vessel was filled with dry petrol-ether, and this was cooled gradually by adding liquid air drop by drop. Substances liquid at ordinary temperatures can easily be melted by bringing a metal wire into the neck of the crystallisation vessel. By withdrawing it more or less high up in the neck of the bottle, crystallisation is again brought about at varying speeds. Crystallisation of the liquid can in this way easily be brought about a great number of times in a short period, and growth-structures and the faces of the growing crystals observed under varied conditions.

By observing between crossed nicols and determining extinction angles, double refraction, and the optical character of the crystal zones developed, it is, of course, not always possible to tell exactly to what crystal system the substance belongs, as the crystals of some substances are developed only in one certain crystallographical direction, but in most cases it is possible to bring about crystallisation in different directions by varying the rate and conditions of cooling. In most cases it is therefore possible to make out with certainty whether the substance belongs to either of the following general groups of crystal symmetry: (1) regular (isotropic); (2) tetragonal or hexagonal; (3) rhombic; (4) monoclinic or triclinic.

#### *Nitrogen.*

The apparatus for crystallising nitrogen, as finally adopted, is shown in fig. 2.

The crystallisation vessel (*c.v.*) of quartz glass which has been described above is contained in a small silvered vacuum vessel A, with two slits in the silvering through which the crystallisation vessel is observed by means of a polarisation microscope clamped in horizontal position, an incandescent gas-burner being used for illuminating purposes. The polarising nicol and the analyser of the microscope are connected by a bar, by means of which they can be revolved simultaneously. The interior of the vacuum vessel A, the syphon S and the exterior of the crystallisation vessel are first carefully dried by keeping them connected with the charcoal bulb E

immersed in liquid air. The interior of the crystallisation vessel, and the T- and U-pieces connecting the crystallisation vessel with the gasholder, are likewise exhausted, then filled with pure nitrogen from the gasholder F, again exhausted by means of the mechanical pump, and then kept in connection with the charcoal bulb C, immersed in liquid air. After all moisture has been expelled from the apparatus in this way, the interior of the vacuum vessel A is connected with the mechanical pump through the three-way stopcock *a*, and liquid air previously filtered and quite clear is admitted from the vacuum vessel B, by opening the screw of the syphon S. This syphon is of the kind described by Sir James Dewar\* and used throughout his experiments at low temperatures. The valve of the syphon is then closed by means of the screw and the liquid

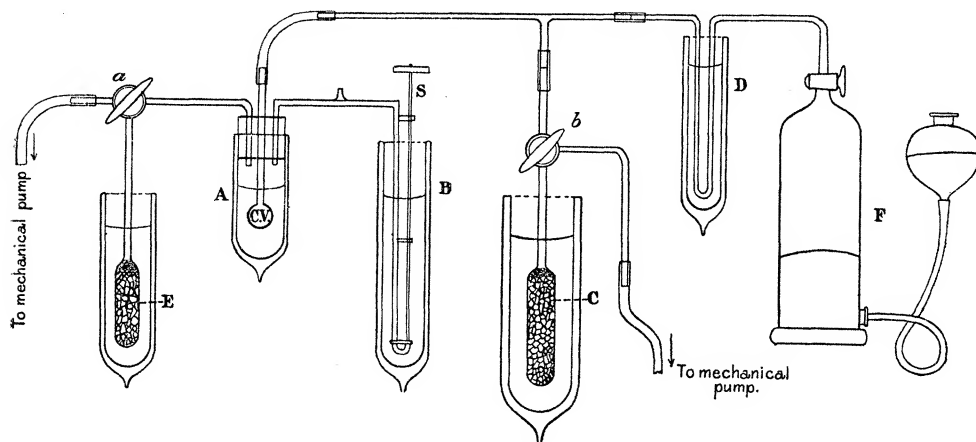


FIG. 2.

air in A exhausted by the mechanical pump. The U-tube D is immersed in liquid air and nitrogen is admitted through it to the crystallisation vessel, where it begins to liquefy as soon as the temperature of the surrounding liquid air has been lowered sufficiently by the exhaust.

When a sufficient quantity of liquid air has been collected in the crystallisation vessel, the gas-holder is closed and the three-way stopcock turned so that the liquid nitrogen is connected with the mechanical pump, or else with the charcoal bulb C. The liquid nitrogen is thereby cooled so much that it either crystallises or becomes a jelly. When crystallised by sudden exhaust a kind of shower of small nitrogen crystals is instantaneously formed, and it is not possible to make out the crystallographic properties of these, as they, even in so thin a layer, form an opaque mass.

\* Dewar, 'Roy. Inst. Proc.,' January, 1901, p. 7, fig. 1.

By closing off the charcoal exhaust and opening the stopcock *b*, the crystal mass is caused to begin to melt, and may then again be crystallised by connecting the mechanical pump with the vessel containing the half-molten mass. By manipulating the three-way stopcock regulating the exhaust on the nitrogen, it is possible to melt and crystallise the nitrogen, and in this way one sometimes succeeds in producing a homogeneous transparent crystal growth, and may observe the fringe of the growing crystals.

In the preliminary experiments nitrogen prepared from air was used, and later, when the method was found to work, a quantity of nitrogen was prepared in the way described by Lord Rayleigh, by treating a solution of potassium nitrite and ammonium chloride on the water-bath and passing the gas over red-hot, previously reduced copper, and subsequently through potash, concentrated sulphuric acid, and over phosphorus pentoxide.\* After the influence of the state of purity of the gas upon the readiness with which good crystals may be obtained had been noticed in the course of the investigation of methane, the nitrogen prepared in the above way was liquefied and fractionated, a middle fraction being collected over mercury and used for these crystallisation experiments.

In those instances where crystallisation took place at a slow rate and large transparent crystal fields were formed, it was easy to study the behaviour of the crystal-film towards polarised light. It was found to be entirely dark between crossed nicols in all positions of the nicols, that is isotropic. Nitrogen thus crystallises in the regular crystal system. This result is also confirmed by the observation, in a few instances, of the formation of crystal growth-structures in which the branches grew at right angles to each other.

In the periodic system of elements nitrogen is the first member of a vertical row in which the other members are known to occur in several polymorphic modifications. The modifications existing at the lowest temperature, of both phosphorus and arsenic, white phosphorus and yellow arsenic, are regular, and so is probably also yellow antimony. Thus the crystal symmetry of nitrogen is in harmony with that of the other members of the same vertical group at low temperatures.

#### *Argon.*

In the case of the crystallisation of argon only the parts A and B of the apparatus shown in fig. 2 were necessary. The crystallisation vessel was connected to the gasholder containing the argon by an intermediary T-piece through which the apparatus was exhausted before the argon was admitted to the crystallisation vessel.

\* Rayleigh and Ramsay, 'Phil. Trans.,' 1895, A, vol. 186, p. 187.

It is sufficient to have a small quantity of liquid air at the bottom of the vacuum vessel, A, and thus cool the crystallisation vessel in the vapour of the air evaporating under reduced pressure. When this small quantity of liquid air evaporates under diminished pressure, it rapidly gets richer in oxygen and the temperature gradually rises correspondingly. By admitting fresh air, richer in nitrogen, through the syphon the temperature is again lowered, and by continuously allowing a small quantity of fresh liquid air to enter the vacuum vessel A, through the syphon, the temperature can be kept close to that of the melting point of argon  $-187.9^{\circ}$ .\*

The melting point and boiling point of argon are only  $1.8^{\circ}$  apart, and the liquefaction, crystallisation, and melting of the argon can therefore be effected simply by regulating the screw valve of the syphon as explained above. It is, therefore, easier to make observations on the crystallisation of argon than on that of nitrogen. The only difficulty arises from the circumstance that the boiling point and melting point of argon are so close to each other at ordinary pressures. A crystallisation vessel of 10 mm. diameter of disc, and about 3 mm. diameter of neck-tube was used, and less than 10 c.c. of argon was required for the investigation.

Crystallised argon is isotropic. Argon thus crystallises in the regular crystal system. The crystals grow very rapidly and usually in the form of very fine growth-structures with a great number of branches.

#### *Methane.*

The apparatus for investigating the crystallisation of methane was the same as used for argon. Methane condenses to the liquid state at  $-164^{\circ}$ , and its melting point,  $-185.8^{\circ}$ , is very close to that of argon.† The crystallisation and melting could therefore be effected as described in the case of argon, simply by regulating the amount of nitrogen-rich liquid air admitted to the vacuum vessel by means of the screw valve of the syphon. As methane condenses to liquid at a much higher temperature than argon, the crystallisation phenomena could be much more easily studied in the case of methane.

The methane used for the investigation was prepared by heating a mixture of sodium acetate and barium oxide and passing the gas twice through caustic potash and concentrated sulphuric acid. The liquefied gas, however, did not crystallise well, and as part of the gas remained uncondensed when cooled in liquid air, and a small amount of crystals were formed even at a temperature near the boiling point of oxygen, it was thought that the gas

\* Ramsay and Travers, 'Zeitschr. f. Phys. Chemie,' 1901, vol. 38, p. 641.

† Olszewski, 'Compt. Rend.,' vol. 100, p. 970.

contained a not negligible amount of hydrogen and higher hydrocarbons of the methane series. The gas was therefore purified by liquefying it and fractionating the liquefied part, the middle fraction being collected in a gas-holder over mercury, and employed during the further experiments.

This pure methane crystallised very readily when cooled with liquid air under exhaust. Crystallisation usually sets in simultaneously from a great many centres and beautiful spherulites are rapidly developed. By partly melting the crystallised layer between the discs of the crystallisation vessel, and causing it to crystallise again, a linear crystallisation front is obtained which grows and moves uniformly over the field of the microscope. The more slowly the cooling is done, the more slowly the crystals grow, and the coarser are the branches of the growth-structures; the more rapid the crystallisation, the finer the growth-structures produced.

The growth-structures of methane are always developed according to the hexahedron and greatly resemble those of ammonium chloride. The crystals are isotropic. Methane therefore also belongs to the regular system.

#### *Ethyl Ether.*

Ether was brought into the same crystallisation vessel which previously had been used for the crystallisation of argon and methane. The liquid was sucked into the narrow space between the quartz-glass discs, and the crystallisation vessel cooled in the manner already described.

Ether crystallises readily, in long well-developed prismatic needles which exhibit vivid interference colours between crossed nicols. The extinction is always parallel to the crystal axis. The double refraction of the prismatic zone is about 0.030. Judging from these data, the absence of isotropic sections, and the way the growing prisms are terminated by two flat dome faces, ethyl ether belongs to the rhombic system.

#### *Ethyl Alcohol.*

When ethyl alcohol is cooled in the crystallisation vessel it gradually becomes thick and sticky, and finally, at the temperature of liquid air, glassy. If the crystallisation vessel, however, is slowly warmed and the inner side of the vessel scratched with a metal wire when the alcohol glass begins to get soft, crystallisation occasionally takes place. The crystals grow as numerous small spherulites in the sticky alcohol, and the rate of growth is extremely slow. With regard to the power of crystallisation, ethyl alcohol thus belongs to the same group of substances as certain silicates and borates, which on cooling are more easily obtained glassy than crystallised. The individual crystals of the spherulites which are obtained show vivid inter-



ference colours between crossed nicols, but on account of their smallness it is not possible to determine if alcohol belongs to the rhombic, monoclinic, or triclinic system.

*Acetone.*

Acetone crystallises in long prismatic crystals which belong either to the monoclinic or triclinic crystal system. The double refraction in the prismatic zone is strong, about 0.030—0.035.

When the liquid is cooled it is generally at first super-cooled, and when crystallisation sets in, the prismatic crystals growing from a common germ, grow with almost instantaneous velocity across the whole crystallisation vessel. If part of the crystals are melted by inserting a metal wire in the crystallisation vessel as described, and the wire is then withdrawn, crystallisation takes place at a temperature only slightly lower than that of the melting point. As in the case with a liquid crystallising in a narrow tube, the rate of growth is constant for a certain distance, and the velocity of crystallisation can be determined with the aid of a micrometer eyepiece and stop-watch. The values obtained are remarkably constant. They are of course not absolute values, but may in any case be regarded as indicating the degree of rapidity with which a substance crystallises at these low temperatures. The value obtained for acetone is 5.3 mm. per minute.

*Methyl Alcohol.*

Methyl alcohol crystallises well, forming prismatic needles belonging to the monoclinic or triclinic crystal systems. The double refraction is about 0.020—0.025. The velocity of crystallisation in the thin film at temperatures close to the melting point is 2.1 mm. per minute.

When the temperature is lowered by cooling with liquid air, these long prismatic crystals of high double refraction change into another crystal modification, which is developed in the form of small needles showing low interference colours. On raising the temperature, the strongly double refracting modification again appears before melting. Methyl alcohol thus occurs in two polymorphic modifications which change enantiotropically into each other.

*Carbon Disulphide.*

Carbon disulphide crystallises in the form of spherulites, and on melting and recrystallisation, when crystals are already present, in the form of long needles. The crystals belong to the monoclinic or triclinic system, more probably to the triclinic. The velocity of crystallisation in the thin film is 3 mm. per minute at temperatures not much below the melting point,

but rises rapidly with decrease of the temperature, and takes place with almost instantaneous velocity when the crystallisation sets in after the liquid has been to some extent super-cooled.

*Summary of Results.*

A quartz glass vessel, holding a very thin layer (0.05 mm.) of substance between polished quartz-glass plates, has been constructed. In this vessel N, A, CH<sub>4</sub>, etc., have been crystallised and investigated crystallo-optically :—

- (1) Nitrogen crystallises in the regular system.
- (2) Argon is regular.
- (3) Methane is regular.
- (4) Ethyl ether is rhombic. Ethyl alcohol, acetone, methyl alcohol, and carbon disulphide are monoclinic or triclinic. Methyl alcohol occurs in two polymorphic forms, changing reversibly into each other.

The experiments described have been made in the Davy–Faraday Research Laboratory of the Royal Institution.

My thanks are due to Prof. Sir James Dewar for kindly lending me the vacuum vessels and charcoal condensers, and placing the necessary quantities of liquid air at my disposal.

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